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DYNAMICS OF THE CHEMISTRY OF ELECTRONICALLY EXCITED ATOMS IN DE--ETC(U)

APR 77 J WIESENFELD

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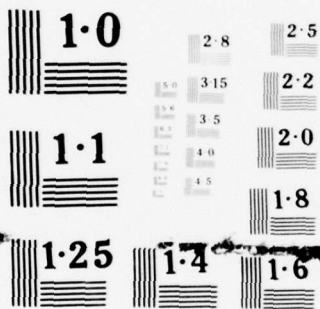
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The deactivation of $I(5^2P_{1/2})$ by HBr and DBr has been shown to proceed via chemical reaction to form HI or DI + $Br(4^2P_{3/2})$. The corresponding deactivation by Br_2 appears to result in the production of electronically excited $Br(4^2P_{1/2})$ as the result of an adiabatic reaction, suggesting the possible construction of a chemically pumped bromine atom laser. The photodissociation of Br_2 has also been investigated and relative intensities of transitions into the $B^3\Pi_0^+$ and $1^1\Pi_{1u}$ states determined.		

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 $B_2 3p \pi_0^+ u$

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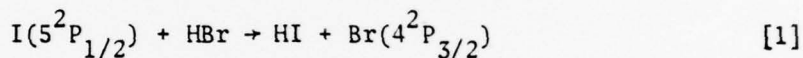
Personnel

The experimental program described here was carried out by two graduate research assistants, Gary L. Wolk and Theodore G. Lindeman. In addition, Mr. William Ebenstein, an undergraduate student, has assisted in these studies.

Experimental Program

The results of our investigation of $\text{Br}(4^2\text{P}_{1/2})$ deactivation by the hydrogen isotopes¹ were discussed in our previous annual report covering the period 4/1/75-3/31/76. A reprint describing this work is attached to the present report.

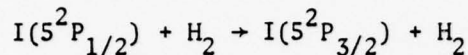
We have continued our study of the chemistry of electronically excited halogen atoms with an investigation of the reaction



where process [1] represents non-adiabatic chemical reaction and [2] corresponds to physical quenching, presumably accompanied by E-V energy transfer. Previous experiments² indicated that the overall deactivation of $\text{I}(5^2\text{P}_{1/2})$ by HBr was far too efficient to be accounted for by the long-range interaction model³ that was successful for predicting the rate of other E-V processes. The suggestion that [1] might play a significant role in this deactivation² was, however, seemingly at variance with the simple one-electron molecular orbital model proposed by Moore and coworkers⁴ for the Br-H-I system. This model predicts that the interaction of $\text{I}(5^2\text{P}_{1/2})$ with HBr would be repulsive in nature, thus precluding a close approach leading to chemical reaction.

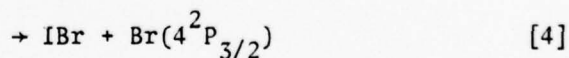
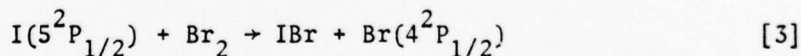
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The experimental procedure is described in the attached manuscript. Briefly, the yield of ground state iodine atoms, $I(5^2P_{3/2})$, following the known quenching



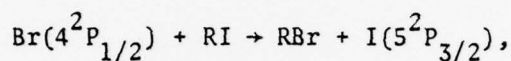
is compared to that obtained following deactivation of $I(5^2P_{1/2})$ by HBr and DBr. Our results clearly demonstrated that deactivation of the excited atom by both of the diatomics is dominated by reaction [1], energy transfer playing at most a very minor role. Consideration of the vibrationally excited virtual states correlating with $I(5^2P_{3/2}) + HBr(v=n)$ suggests that the reaction takes place via a concerted process involving an avoided crossing from a surface correlating with $I(5^2P_{1/2}) + HBr(v=0)$ to that correlating with $I(5^2P_{3/2}) + HBr(v=4)$. The decrease in efficiency associated with collisional deactivation by DBr may then be explained in terms of a smaller matrix element associated with the $DBr(v=0) \rightarrow DBr(v=5)$ process.

While this system suggests that the one-electron model must at least be modified, further investigations in this laboratory indicate that its general applicability must be carefully reviewed. In particular, we have measured the rate of $I(5^2P_{1/2})$ removal by Br_2



and find $k_{3+4+5} = 1.8 \times 10^6 \text{ torr}^{-1} \text{ sec}^{-1}$. Following infra-red chemiluminescence experiments by Houston⁵ who observed emission from $Br(4^2P_{1/2})$

following deactivation of $I(5^2P_{1/2})$ by Br_2 , we monitored the population of ground and excited state bromine atoms in this system. Our preliminary measurements clearly show that deactivation of $I(5^2P_{1/2})$ by Br_2 proceeds predominantly by adiabatic reaction [3] to produce electronically excited bromine, $Br(4^2P_{1/2})$. This observation cannot be reconciled with the one-electron *m-o* model as no energetically accessible potential surface would be predicted. More complete details concerning this interesting system will be obtained in future experiments which will take into account complicating side reactions such as



which currently preclude detailed analysis of the observed kinetics.

In conjunction with our investigation of halogen atom reaction kinetics, we have also undertaken an examination of the photolysis of simple halides. Currently, we are examining the photodissociation of alkyl bromides, namely CF_3Br and CH_3Br , following exposure to a pulsed black-body light source. We have observed the relative quantum yields of $Br(4^2P_{1/2})$ and $Br(4^2P_{3/2})$ to be a very strong function of substituent as shown below

$\phi = [x(n^2P_{1/2})]/[x(n^2P_{3/2})]$		
R group	x=Br	x=I (ref. 6)
CF_3	20	10
CH_3	<u><1</u>	11.5

the data on alkyl iodides being included for comparison. The strong dependence of branching ratio, ϕ , on the substituents displayed by the bromides is striking and may be related to the spin-orbit splitting

observed in the bromide which is much smaller than that characterizing the iodide.

The acquisition of a larger pulsed dye laser has permitted the laser-induced photodissociation spectroscopy (LIPS) experiment to yield significant results. In particular, the photodissociation spectrum of Br_2 has been investigated with a view toward obtaining the relative absorptivities from the $\text{Br}_2(X^1\Sigma_g^+)$ ground state into the two excited states, $^1\Pi_{1u}$ and $B^3\Pi_{0u}^+$. The initial experiments are described in the attached manuscript which is being presented at the Lasers in Chemistry Conference at the Royal Institution in London. These experiments involved the use of an untuned laser and as a result, detailed information concerning the relative absorptivities in the region near $22,000\text{ cm}^{-1}$ where they cross was not obtained. Our preliminary results are in reasonable agreement with those obtained from the temperature-dependence of the Br_2 absorption spectrum⁷.

Planned Research

Our experimental program in the present contract period will be greatly enhanced by the acquisition of a minicomputer system which will be used as a sophisticated data analysis tool. The availability of such a device will permit the direct reduction of non-exponential temporal profiles, a process which currently must be estimated in a variety of error-prone and time-consuming techniques. The present signal averager-desk calculator will remain in very active use, however.

As indicated above, the use of a grating and/or etalon to tune our dye laser will be of great utility in the LIPS experiments. The critical region of the Br_2 spectrum will be investigated fully in order to resolve the visible absorption band. We shall then concentrate on the photolysis

of IBr which, due to the lower symmetry, displays significant spectral perturbations due to avoided crossings. Of particular interest will be the potential of creating a population inversion in iodine atoms, following the photolysis of IBr near 420 nm.

The experimental program involving halogen atom chemistry will also be actively pursued especially with regard to understanding the reactivity of these species in defined quantum states. The $I(5^2P_{1/2}) + Br_2$ system described earlier will be of primary concern. We shall also install the temperature-controlled reaction vessel which has been constructed to further probe the details of the potential surfaces which control the behavior of halogen atoms in the gas phase.

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LASER INDUCED PHOTODISSOCIATION SPECTROSCOPY: HALOGENS AND INTERHALOGENS

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Abstract

The continuous absorption spectra of small molecules have been examined using Laser Induced Photodissociation Spectroscopy (LIPS). In this technique, molecules are photolyzed using a flashlamp-pumped tunable dye laser; the atomic products of the dissociation are then monitored by time-resolved resonance absorption spectroscopy in the vacuum ultraviolet. Results obtained by LIPS for the molecule Br_2 will be discussed with an emphasis on the measurement of the wavelength-dependent relative absorptivities into the excited states, $^3\pi_0^+u$, $^1\pi_{1u}$.

Introduction

The spectra and electronic structure of halogen molecules have been extensively investigated [1]. The information obtained about the low-lying excited states of these molecules has led to the development of our understanding of the spectroscopic basis of photochemistry. While most experimental observations have been carried out on I_2 , the other halogens have also been investigated. In particular, the spectrum of Br_2 has been studied, [2] both in the bonded region below the thermochemical threshold for formation of $\text{Br}(4^2P_{1/2}) + \text{Br}(4^2P_{3/2})$, $19,580 \text{ cm}^{-1}$, and more recently in the continuum region where the significant transitions are $\text{Br}(^3\pi_0^+u) + \text{X}^1\Sigma^+$ and $^1\pi_{1u} + \text{X}^1\Sigma^+$, the $^3\pi_0^+u$ state correlating with $\text{Br}(4^2P_{1/2}) + \text{Br}(4^2P_{3/2})$ and the $^1\pi_{1u}$ with $^3\pi_0^+u$ $\text{Br}(4^2P_{3/2})$.

The experiments on Br_2 spectroscopy have not, in general, been accompanied by corresponding quantitative investigations of halogen photochemistry. In particular, the actual yields of $\text{Br}(4^2P_{1/2})$ and $\text{Br}(4^2P_{3/2})$ following the photolysis of Br_2 have only recently been reported for a set of discrete photolytic wavelengths [3]. These experiments were carried out using the elegant technique of photo-fragment spectroscopy, where both the translational energy and the angular distribution of photolysis products with respect to the polarization of the incoming actinic radiation are obtained. Analyses of these data yield both the relative efficiencies for the production of specific quantum states of the atom as well as the symmetry of the spectroscopic transition leading to photodissociation. Although measurements of the relative yields of electronically excited and ground state Br atoms have been made at relatively few wavelengths, it appears that substantial disagreement exists between results obtained by direct observation of products [3] and those derived from analysis of the temperature-dependence of the Br_2 absorption spectrum [2]. The experiments described here were carried out in order to resolve this discrepancy and to test the validity of the spectral analysis method.

Experimental

Figure 1 is a schematic diagram of the apparatus used for laser induced photo-

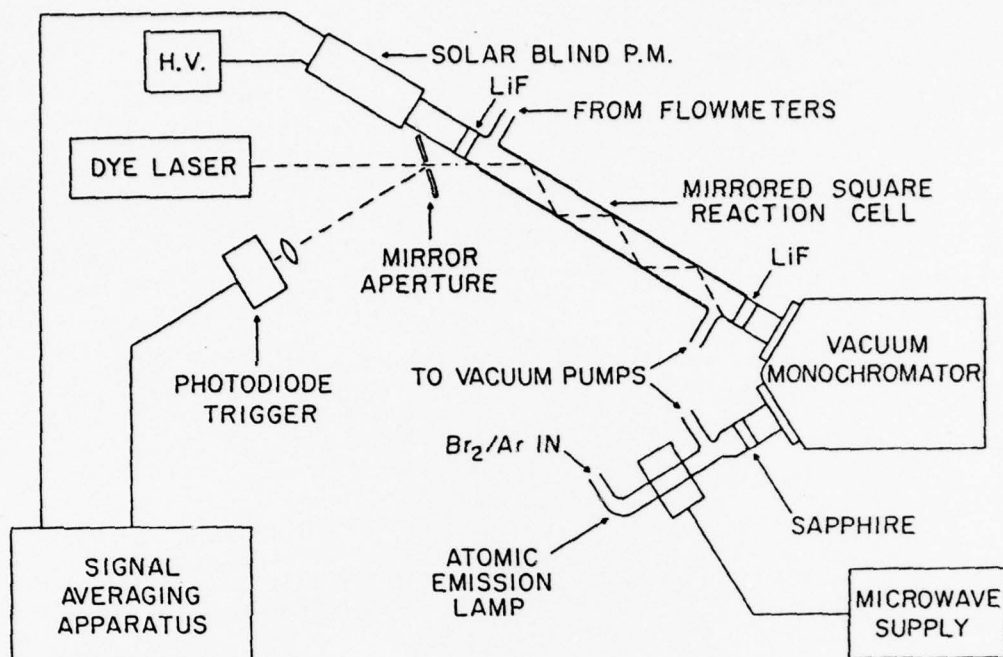


Figure 1. Schematic diagram of experimental apparatus.

dissociation spectroscopy (LIPS). The photolysis of the source molecule was accomplished in a 20 cm Pyrex vessel with an internal square cross-section of 1.0 cm. The output of the laser beam was directed through the vessel, whose polished walls were externally coated with an Al film. Approximately 20-25 reflections were made as the light was transmitted through the length of the square cell, resulting in a total pathlength of ca. 28 cm. The Br₂ source gas was present in a very dilute solution with Ultra High Purity Argon (Matheson) which was passed over molecular sieve at 195°K immediately prior to use. The argon served both as a thermal buffer and to slow the rate of atomic diffusion to the walls of the vessel. The gases in the reaction cell were swept out in a time short compared to the period between laser pulses (3-8 Sec) but long compared to the characteristic time for diffusion (ca. 20 mSec).

The dye laser (Model 1200, Phase-R) was pumped by a fast coaxial flashlamp and produced output pulses of 100-200 nS duration. A number of dyes (Table 1) were utilized in these experiments in order to permit observation of photodissociation products following exposure to a range of actinic wavelengths. The laser cavity consisted of two broad band mirrors; in these initial experiments no effort was made to tune the laser over narrow spectral regions. Output energies of 10-30 mJ were achieved with the dyes listed; the relatively modest power levels attained, i.e., ~100 KW suggest that two-photon processes should not play a significant role in these experiments.

The temporal profiles of ground state, Br($4^2P_{3/2}$) \equiv Br, and electronically excited, Br($4^2P_{1/2}$) \equiv Br*, bromine atom concentrations were monitored using time-resolved atomic absorption spectroscopy. The atomic resonance radiation was

produced in a microwave-powered electrodeless discharge lamp through which flowed ca. 0.3 torr of a 1% Br₂/Ar mixture. Incident power was 18 W. The output of the resonance lamp (Figure 2) was then dispersed using a 0.3 M vacuum monochromator (McPherson 218) and detected by an EMI G26E3-15 solar blind photomultiplier. The ground and excited states of bromine were detected by attenuation of the resonance transitions, 5²P_{3/2} + 4²P_{3/2} (148.9 nm) and 5²P_{1/2} + 4²P_{1/2} (153.2 nm), respectively. Transient absorption signals following the laser pulse were digitized using a Biomation 802 Transient Recorder and then averaged to enhance the observed signal-to-noise ratio. Typically 16-64 kinetic runs were averaged.

Ultrapure Br₂ (99.9%, Ventron) was extensively degassed. Research grade H₂ (Matheson) was used as received. All mixtures were prepared on a mercury-free vacuum system, evacuable to 10⁻⁶ torr and equipped with a capacitance manometer and stainless steel test gauges. The partial pressures of reagents in the photolysis cell were determined from the total pressure (20-35 torr) and relative flow rates measured with calibrated rotameters. The pressure of Br₂ varied in the range 0.008-0.030 torr; that of H₂ was either 0 or between 0.040 and 0.10 torr.

Results and Discussion

In order to test the experimental arrangement described above, the overall rate of Br* deactivation upon collision with Br₂ was determined. This was accomplished by monitoring the 153.2 nm resonance line following laser photolysis of Br₂. The absorption of resonance radiation may be related to the concentration of Br* atoms through the use of the Beer-Lambert Law

$$\ln(I_0/I)_t = \epsilon(l[X])^\gamma$$

where X = Br*. The value of the exponent, γ , which relates the observed transmission to the relative atomic concentration is determined experimentally [4] to be 1.0 in this apparatus. The measurement of k_{Br_2} was carried out by determining

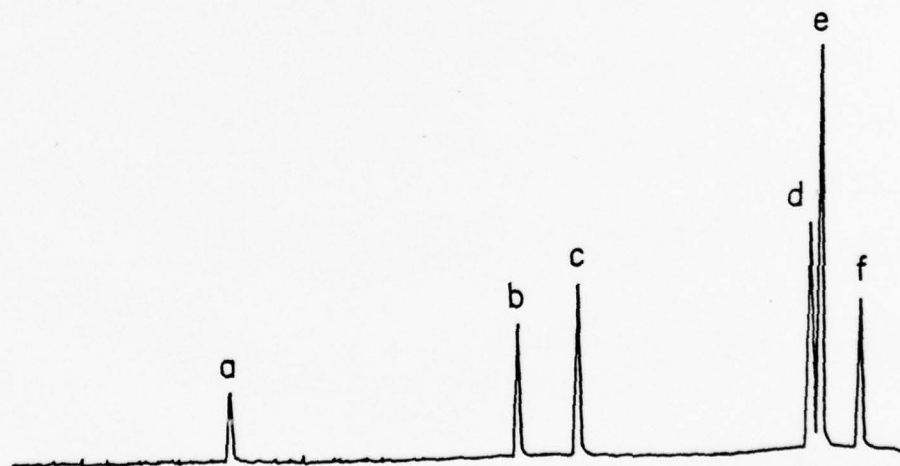


Figure 2. Output spectrum of bromine resonance lamp. Transitions at 148.9 (a) and 153.2 (b) nm were used in these experiments. See text.

the pseudo-first order rate coefficients, k , for Br^* deactivation in an excess of Br_2 ($P_{\text{Br}_2} = 0.008\text{--}0.020$ torr). The rate coefficient for Br^* removal is given by

$$k = k_{\text{Br}_2} [\text{Br}_2] + K$$

where K represents impurity quenching and diffusion to and deactivation at the walls of the photolysis cell. The value of k_{Br_2} obtained in these experiments, $1.1 \pm 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ compares very favorably with the values in the range $1.0\text{--}1.2 \times 10^{-12}$ reported in infra-red emission [5] experiments. An earlier measurement [6] made using photographic kinetic spectroscopy yielded $k_{\text{Br}_2} = 2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, in poor agreement with more recent data.

The determination of relative absorptivities for absorption via the $\text{Br}^3\pi_0 + \text{X}^1\Sigma^+$ and $\text{Br}^1\pi_u + \text{X}^1\Sigma^+$ transitions, $\epsilon(^3\pi)/\epsilon(^1\pi)$, was made by measuring the relative yields of Br^g and Br^* following flash photolysis at a specific wavelength. The relative concentration of ground state bromine atoms was monitored at 148.9 nm under two experimental conditions. First, the temporal profile of bromine concentration, $[\text{Br}]_t$, was obtained in the absence of any added quencher of Br^* . As may be seen from Figure 3a, this profile is characterized by a very rapid rise in Br concentration coincident with the laser pulse. This represents photolytic production of Br atoms from Br_2 . The relatively level period then may be ascribed to physical quenching of Br^* by Br_2 to form Br . This occurs on approximately the same time scale as diffusion of Br to the walls of this small photolysis vessel. This latter removal process dominates the Br -atom profile at long times, and results in heterogeneous recombination to form Br_2 . Direct measurement of the absorption transient immediately following the laser pulse thus provides a relative photolytic yield of Br atoms.

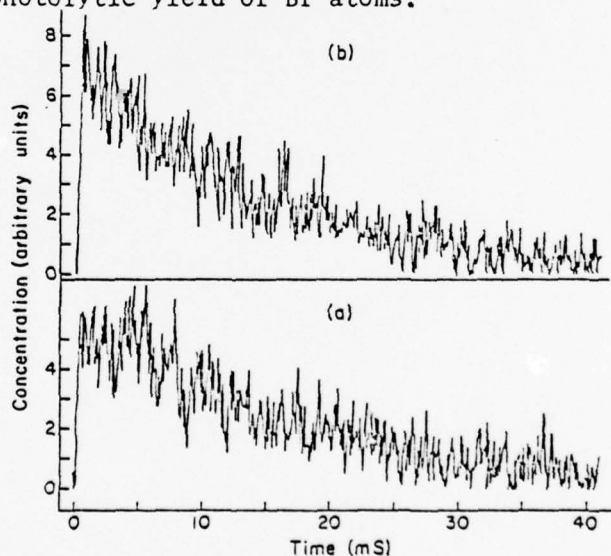


Figure 3. Br -atom profiles following laser photolysis of Br_2 at 21010 cm^{-1} .
 $p_{\text{Br}_2} = 0.012$ torr, $p_{\text{Ar}} = 19$ torr.
 a) $p_{\text{H}_2} = 0$
 b) $p_{\text{H}_2} = 0.039$ torr
 Each trace represents average of 32 experimental runs.

The photolytic production of Br^* is then determined by addition of 0.040-0.10 torr of H_2 to the photolysis vessel. This results in the deactivation of Br^* on a time scale (ca. 15-20 μS) rapid with respect to that of the transient measurement (Figure 3b). As deactivation of Br^* by H_2 results in the quantitative production of ground state Br atoms (chemical reaction to form $\text{H} + \text{HBr}$ is 6.2 kcal endothermic), the initial absorption at 148.9 nm represents the total photolytic yield of ground and excited bromine atoms, $[\text{Br}^*]_{t=0} + [\text{Br}]_{t=0}$. As the partial pressure of Br_2 and laser energy (and hence $[\text{Br}]_{t=0}$) remain constant, it is possible to obtain $[\text{Br}^*]_{t=0}$ by application of the modified Beer-Lambert Law noted above.

The photolysis of Br_2 following excitation into the $^3\pi$ state above the dissociation threshold results in the production of $\text{Br}^* + \text{Br}$ while excitation into $^1\pi$ yields two Br atoms. The $\text{A}^3\pi_{1u} \leftarrow \text{X}^1\Sigma_g^+$ transition appears from spectroscopic data [2] to play no role in the violet-blue region of the Br_2 absorption spectrum. The relative absorptivities into the $^3\pi$ and $^1\pi$ continua may thus be related to the observed ground and excited-state Br atom yields,

$$\frac{\epsilon(^3\pi)}{\epsilon(^1\pi)} \propto \left[\frac{[\text{Br}]_{t=0}}{2[\text{Br}^*]_{t=0}} - 0.5 \right]^{-1}$$

The results obtained by application of this equation to experimental data taken at several photolysis wavelengths are presented in Table 1. The values of $\epsilon(^3\pi)/\epsilon(^1\pi)$ are in sensible agreement with those derived from inspection of resolved spectral curves presented in previous reports [2,3]. Several points deserve more detailed discussion. The production of Br^* following photolysis of Br_2 at $18350 \pm 250 \text{ cm}^{-1}$ cannot be due to direct photodissociation. Rather, its appearance may reasonably be ascribed to the effect of a collisional release process involving highly vibrationally excited $\text{Br}_2(\text{B}^3\pi_{0u})$ which undergoes essentially thermal dissociation upon collision with Br_2 or Ar [7]. This phenomenon plays a significant role only in the region near the thermochemical threshold for production of $\text{Br} + \text{Br}^*$; it need not be considered for photolysis above this energy.

The photolysis of Br_2 immediately above the dissociation threshold is dominated by excitation into the $\text{B}^3\pi_{0u}$ state. This observation is in good agreement with previous spectral measurements [2] suggesting that the major component of the

Table 1

Relative Absorptivities for $\text{B}^3\pi_{0u} \leftarrow \text{X}^1\Sigma_g^+$ and $^1\pi_{1u} \leftarrow \text{X}^1\Sigma_g^+$ Transitions in Br_2

Laser Dye	$\nu \text{ (cm}^{-1}\text{)}$	$\epsilon(^3\pi)/\epsilon(^1\pi)$
P495	18350 ± 250	0.4
Coumarin 102	21010 ± 275	13
Coumarin 2	22125 ± 100	1.8

low energy maximum in Br₂ absorption near 20500 cm⁻¹ is due to B³π₀⁺ + X¹Σ_g⁺. The dominance of this transition rapidly decreases at higher energies and, as may be seen from the data collected at 22125 cm⁻¹, the ¹π_{1u} + X¹Σ_g⁺ transition becomes the major component of the absorption below ca. 455 nm. The large change in the observed ε(³π)/ε(¹π) ratio over a short wavelength range, namely 475-452 nm suggests that similar experiments to those carried out here but involving a tunable laser cavity will yield significant information concerning the individual components of the absorption band. Such investigations are currently under way in this laboratory.

In addition, preliminary studies of the photodissociation of IBr are also in progress. We hope to obtain the yields of both ground and excited states of iodine and bromine atoms as a function of excitation wavelength in order to elucidate the nature of the higher-lying potential curves characterizing this molecule.

Acknowledgment

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* Henry and Camille Dreyfus Teacher-Scholar.

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Deactivation of $I(5^2P_{1/2})$
by Chemical Reaction with HBr and DBr

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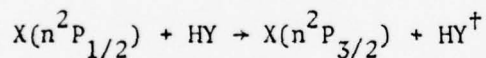
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Abstract: The collisional deactivation of electronically excited iodine atoms, $I(5^2P_{1/2})$, by CH_4 , C_3H_8 , HBr and DBr has been investigated using time-resolved atomic resonance spectroscopy. This technique permits direct determination of the yield of $I(5^2P_{3/2})$ following the deactivation of the excited atoms by the added gas. The experiment demonstrated that the deactivation of $I(5^2P_{1/2})$ by CH_4 and C_3H_8 proceeds by physical quenching, but deactivation by HBr and DBr occurs via metathetical chemical reaction to form $HI + Br(4^2P_{3/2})$. This non-adiabatic reaction is discussed in the context of a curve-crossing model involving vibrationally excited virtual states of the deactivating molecule.

Deactivation of $I(5^2P_{1/2})$ by Chemical Reaction with HBr and DBr

Investigations of the collisional deactivation of electronically excited halogen atoms have played a significant role in the elucidation of those chemical and physical processes which govern the behavior of electronically excited species in the gas phase. Thus, the overall rate coefficients for deactivation of $X(n^2P_{1/2})$, where $X = Cl, Br$ or I have been measured¹⁻⁹ using a variety of techniques, the difficulty of making such determinations being $I < Br < Cl$.

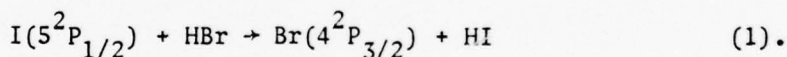
While such a broad collection of data has been useful to the development of a theoretical description of the deactivation of electronically excited halogens, it would appear that a complete understanding of these phenomena must await the analysis of the products of the collisional events. Discrimination between physical energy transfer (with concomitant excitation of internal modes of the quenching molecule and relative translation between products) and actual metathetical chemical reactions resulting in the formation of new molecular products would thus be possible. Recent developments in excited halogen chemistry have included the observation of infrared emission from vibrationally excited hydrogen halides^{3,4,7,8,10} produced following electronic-vibrational (E-V) energy transfer



where $X = Br, I$ and $Y = F, Cl, Br$. These E-V processes have been interpreted in terms of coupling via long-range interactions,¹¹ a process which is greatly facilitated by resonance between the magnitudes of the electronic and vibrational quanta involved.^{12,13} Measurements of overall deactivation efficiencies for spin-orbit relaxation of excited halogens by hydrogen halides and hydrogen

isotopes also appear to indicate that such long-range quadrupole-multipole interactions play a significant role, but theory and experiment do not yet appear to be in full agreement with respect to the relative importance of E-V processes as compared to translational excitation (E-T) of the product species.^{9,14,15}

Direct evidence for chemical reaction as an efficient route for the collisional deactivation of $I(5^2P_{1/2})$ by halogen molecules¹⁶ and nitrosyl halides¹⁷ has been obtained using kinetic spectroscopy. In addition, I-atom abstraction may play a minor role in the deactivation of $I(5^2P_{1/2})$ by alkyl iodides¹⁸⁻²⁰ as does H-atom abstraction to form HI in the deactivation of excited iodine atoms by ethane and propane.²¹ The deactivation of $Br(4^2P_{1/2})$ by HI, which may proceed via thermally accessible adiabatic and non-adiabatic reactive channels to produce $HBr + I(5^2P_{1/2})$ or $HBr + I(5^2P_{3/2})$ respectively, has been demonstrated⁷ to undergo quenching with formation of $Br(4^2P_{3/2}) + HI$. However, Pritt and Coombe⁸ have suggested that the anomalously rapid deactivation of $I(5^2P_{1/2})$ by HBr and HI may be the consequence of non-adiabatic reactions, e.g.,



This would be at variance with the view of Bergmann, et. al.,⁷ who invoked a simple valence-bond model to explain the relative stability of $Br(4^2P_{1/2})$ (with respect to $Br(4^2P_{3/2})$) upon collision with HI. The experiments described below test this model and permit its further refinement.

Experimental

The apparatus utilized in these experiments has been described previously.^{22,23} $n\text{-C}_3\text{F}_7\text{I}$ was used as the source for iodine atoms. A dilute solution (typically $5\text{--}50 \times 10^{-3}$ torr) of $n\text{-C}_3\text{F}_7\text{I}$ in an argon buffer ($p_{\text{total}} = 60$ torr) was exposed to a pulse of light ($t_{1/2} \approx 10 \mu\text{sec}$, $E = 100\text{J}$). Thermalization of species in the quartz reaction vessel was insured by the presence of the argon buffer gas. The temporal profiles of $[I^*]_t$ ($I^* \equiv I(5^2P_{1/2})$) or $[I]_t$ ($I \equiv I(5^2P_{3/2})$) following the flash were monitored by observing the attenuation of atomic resonance radiation at 178.3 nm ($6^2P_{3/2} \leftarrow 5^2P_{3/2}$) or 206.2 nm ($6^2P_{3/2} \leftarrow 5^2P_{1/2}$). The resonance transitions were excited in a microwave powered electrodeless discharge lamp. The lamp contained a small amount of solid I_2 with one torr of argon. The vapor pressure of I_2 in the lamp was controlled by varying the temperature of a cold finger, typically in the range $263\text{--}265^\circ\text{K}$. The transient absorption signal was monitored by using a solar-blind HTV-R116 photomultiplier tube and digitized with a Biomation 802 Transient Recorder. The photomultiplier gain was decreased during the photolytic flash by switching dynodes 5 and 7 to a common voltage. This minimized the magnitude of the scattered light pulse reaching the digitizing electronics and permitted accurate absorption measurements within $25 \mu\text{s}$ following the initiation of photolysis. Typically 8-16 runs were averaged in order to enhance the signal. Gases in the reaction vessel were swept out between individual kinetic runs. The photolysis of HBr or DBr was prevented²⁴ by the introduction of CCl_4 into a 1 cm thick annular filter chamber around the quartz reaction vessel. No decomposition of the CCl_4 was noted during the course of an experimental session.

Samples of $n\text{-C}_3\text{F}_7\text{I}$ (PCR, Inc) were first degassed and then purified by repeated distillations from a chlorobenzene slush (228°K) to liquid N_2 . Research grade H_2 (Matheson) was used without further purification. Ultra High Purity argon (Matheson) was passed over a molecular sieve at 193°K immediately before use. HBr (99.8%, Matheson) was degassed and repeatedly distilled from ethanol slush (159°K) to liquid N_2 . DBr (99 atom % Deuterium, Merck Sharp & Dohme Isotopes) was similarly purified. DBr was also stored at 240°K prior to use. Research grade C_3H_8 (Matheson) was purified by several distillations from ethanol slush to liquid N_2 . Research grade CH_4 (Phillips 66) was thoroughly degassed before use.

All mixtures were prepared on a Hg-free glass vacuum line which was evacuable to $\sim 10^{-6}$ torr. The composition of the gas mixture in the reaction vessel was determined by use of calibrated floating ball rotameters. Pressures were measured with a glass Bourdon gauge and standard test gauges. This vacuum system was exposed to DBr before preparation of mixtures including this gas in order to passivate the exposed surfaces to H-atom exchange.

Results

The initial experimental study described here involved the determination of the overall rate constant at 295°K for the collisional deactivation of I* by the gases H₂, CH₄, C₃H₈, HBr and DBr. The removal of I* was monitored using the resonance transition at 206.3 nm, the absorption signal being related to [I*]_t by

$$\ln I_0/I_t = \epsilon(\ell[I^*]_t)^\gamma \quad (2)$$

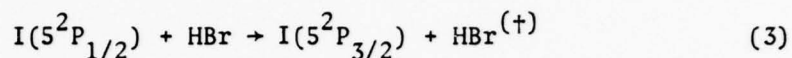
where the constants have previously been described.²⁵ The intensity of the radiation passing through the vessel, I₀, before the flash was obtained using the pretrigger record feature of the Transient Recorder. An experimental value of γ (typically 0.72-0.88) was determined over the range of observed absorption using the technique discussed below. The pseudo-first order rate coefficient, k, derived from the transient absorption measurements ([Q] >> [I*]_t) may be related to the bimolecular rate constant, k_Q, by

$$k = k_Q[Q] + K$$

where K represents removal of I* by spontaneous emission, diffusion to the walls of the reaction vessel and quenching by impurities in the samples of n-C₅F₇I and argon buffer.

The results of these experiments are presented in Fig. 1 and Table I. Inspection of Table I suggests that the current results are in very good agreement with those obtained in other laboratories thus confirming the utility of the modified Beer-Lambert Law (2) in relating the observed transmission of resonance radiation through the reaction vessel to the concentration of transient species present.

Determination of the overall rate constant described above does not yield information concerning the mechanism by which deactivation occurs. Rather, it is necessary to monitor the products of either reaction (1), the chemical removal of I^* by HBr and/or the quenching process

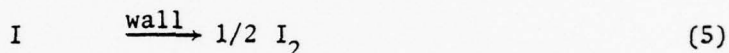


the yield of reaction then being expressed as $\Lambda = k_1/(k_1 + k_3)$. The measurement of Λ was carried out by monitoring the concentration of ground state I at 178.3 nm during the course of the following experiments:

- a. A given pressure of $n\text{-C}_3\text{F}_7\text{I}$ was photolyzed in the absence of all gases other than the argon buffer (Fig. 2a). The absorption measured immediately following the photolytic flash thus represented $[I]_{t=0}$, the amount of ground state iodine atoms produced photolytically.
- b. Addition of an excess of H_2 to the photolysis mixture described in a. resulted in the relatively rapid ($\tau = (k_{\text{H}_2} [\text{H}_2])^{-1} \sim 10^{-3} - 10^{-4}$ sec) relaxation of I^* produced in the flash to form I. It should be noted that collisional deactivation of I^* by H_2 must proceed via quenching to ground state atoms as reaction to form $\text{H} + \text{HI}$ is 11.2 kcal endothermic. Hence, the absorption immediately following the flash (Fig. 2b) may be related to the total production of iodine atoms, $[I^*]_{t=0} + [I]_{t=0}$.
- c. Replacement of the H_2 by HBr (or other deactivating molecule under investigation) so that $k_{\text{H}_2} [\text{H}_2] \approx k_{\text{HBr}} [\text{HBr}]$ permits direct measurement of the ground state iodine atoms produced by quenching of I^* by the HBr in process (3). If the absorption at 178.3 nm is significantly smaller than that obtained following

quenching by H_2 , it may be inferred that a significant fraction of the deactivation proceeds via chemical reaction (1). This is demonstrated in Fig. 2c.

While the results displayed in Fig. 2 clearly show that $k_1 > k_3$, quantitative information must be obtained from a detailed analysis of the kinetic scheme characterizing the transient species present in the reaction vessel. Such a scheme may be represented by



where $k_4 = \beta'/P_{Ar} + A_{nm} + k_Q[Q]$, Q being a trace impurity in the argon buffer. The term β'/P_{Ar} represents deactivation to I following diffusion to the vessel walls. Under the experimental conditions used, processes (1) and (3) would display pseudo-first order kinetics so $k_1' = k_1[HX]$ and $k_3' = k_3[HX]$. The kinetic equations

$$\frac{d[I^*]}{dt} = - (k_1' + k_3' + k_4) [I^*]$$

$$\frac{d[I]}{dt} = (k_3' + k_4') [I^*] - k_5[I]$$

may be integrated yielding

$$[I^*]_t = [I^*]_{t=0} \exp(-(k_1' + k_3' + k_4) t) \quad (6)$$

$$[I]_t = \frac{(k_3' + k_4) [I^*]_{t=0}}{k_5 - k_1' - k_3' - k_4} \left[e^{-(k_1' + k_3' + k_4)t} - e^{-k_5 t} \right] + [I]_{t=0} e^{-k_5 t} \quad (7).$$

Since $k_1' + k_3' + k_4 \gg k_5 \sim \beta'/P_{Ar}$, at times long compared to $(k_1' + k_3' + k_4)^{-1}$

equation (7) reduces to

$$[I]_t \approx e^{-k_5 t} \left\{ \frac{-(k_3' + k_4) [I^*]_{t=0}}{k_5 - k_1' - k_3' - k_4} + [I]_{t=0} \right\}.$$

Thus, a plot of $\ln[I]_t$ vs. time should be linear with slope $-k_5$ and intercept α

$$\alpha = \frac{-(k_3' + k_4) [I^*]_{t=0}}{k_5 - k_1' - k_3' - k_4} + [I]_{t=0}.$$

Such a relationship is indeed observed for the temporal profiles of ground state iodine atom concentrations for the experiments done in the presence of H_2 or other deactivating molecules discussed here. Substitution for k_4 and rearrangement yields

$$\frac{\alpha - [I]_{t=0}}{[I^*]_{t=0}} = \frac{-(k_3' + k_4)}{k_5 - (k_1' + k_3' + \beta' / P_{Ar} + k_Q [Q] + A_{nm})} \quad (8).$$

As noted above $k_5 \sim \beta' / P_{Ar}$. Furthermore, $k_1' + k_3' \gg k_Q [Q] + A_{nm}$. Finally, the numerator of (8) may be simplified by the assumption $k_3' \gg k_4$ which is valid so long as k_3' is not much smaller than k_1' , i.e., some appreciable fraction of the deactivating collisions result in quenching rather than reaction. If reaction is, on the other hand, overwhelmingly predominant the following analysis yields only a lower limit on the true value of Λ .

Equation (8) now becomes

$$\frac{\alpha - [I]_{t=0}}{[I^*]_{t=0}} = \frac{k_3'}{k_1' + k_3'} = 1 - \Lambda \quad (9).$$

Referring to the earlier description of the experimental sequence and recalling the modified Beer-Lambert Law, we define $A_0 = \ln(I_0/I)_{t=0} = \epsilon(\lambda[I]_{t=0})^Y$ as the absorbance immediately following the photolysis of $n-C_3F_7I$ in the absence

of an added quencher, $A_{H_2} = \epsilon(\ell([I]_{t=0} + [I^*]_{t=0}))^\gamma$ as the absorbance measured in the presence of H_2 and $A_{HX} = \epsilon(\ell\alpha)^\gamma$ as the absorbance determined in the presence of a potential reactant. Substitution into (9) now yields

$$\Lambda = 1 - \frac{A_{HX}^{\gamma-1} - A_o^{\gamma-1}}{A_{H_2}^{\gamma-1} - A_o^{\gamma-1}} \quad (10).$$

The averaged values of Λ summarized in Table II were obtained by evaluating the experimental absorbances at 178.3 nm following photolysis of $n-C_3F_7I$ in the absence of any added quencher, with H_2 and with HX . A given set of three runs were included in the overall average if the partial pressure of $n-C_3F_7I$ was maintained to $\pm 1 \times 10^{-3}$ torr. As noted previously,²⁵ in the limit where the $n-C_3F_7I$ may be regarded as an optically thin absorber and the concentration of ground and excited state iodine atoms produced in the flash is proportional to the partial pressure of $n-C_3F_7I$,

$$[I^{(*)}]_{t=0} = \kappa \cdot P_{n-C_3F_7I}^{(*)} \quad (11)$$

(κ reflects the photolytic yield of iodine atoms), substitution of (11) into (2) yields

$$\ln \ln(I_o/I)_{t=0} = \text{constant} + \gamma \ln P_{n-C_3F_7I} \quad (12).$$

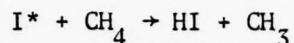
Plots of $\ln A_x$ where $A_x = A_o, A_{H_2}$ or A_{HX} vs. $\ln P_{n-C_3F_7I}$ derived from the present experimental data (Figs. 3-6) verify this relationship over the range of absorbances measured as well as yielding required values for γ used in the evaluation of (10). It may further be shown that

$$\Lambda = 1 - \frac{(\exp(\Omega_{HX}/\gamma) - \exp(\Omega_o/\gamma))}{(\exp(\Omega_{H_2}/\gamma) - \exp(\Omega_o/\gamma))} \quad (13)$$

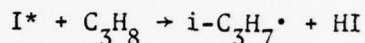
where Ω_x is the constant in (12). Evaluation of (13) leads to values of Λ in good agreement with those obtained by use of (10), but errors introduced by slow long-term drifts in flash lamp output and resonance lamp profile which are avoided by calculating Λ using data points collected over a short period of time leads to a larger scatter in the final results.

Discussion

The examination of CH_4 and C_3H_8 as deactivating gases was carried out in order to assess the precision of the experimental technique outlined above. Neither of these gases is expected to react appreciably with I^* , hydrogen abstraction from CH_4 ,

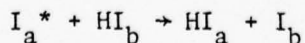


being 11.0 kcal endothermic. Abstraction of a secondary hydrogen from C_3H_8

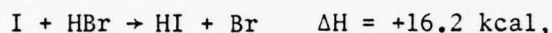


is 1.5 kcal endothermic and photochemical investigations have shown²¹ $\Lambda < 0.01$ for this reaction. The values reported here suggest a limit on the precision of the method, namely, 10-20%. Thus, it is unlikely that deactivation processes with $\Lambda < 0.1$ may reliably be examined using the present technique.

As noted above, the large values of Λ associated with the deactivation of I^* by HBr and DBr must be regarded as a lower limit due to the approximation made in the derivation of (9), i.e., $k_3' \gg k_4$. Nonetheless, it is clear from these experiments that $k_1 \gg k_3$ and chemical reaction dominates the deactivation of I^* by HBr and DBr . This observation corroborates the earlier suggestion⁸ that models based on long-range interactions cannot account for the efficiency of the overall collisional deactivation of the electronically excited iodine atom. Similar chemical processes have been invoked¹ to explain the relatively efficient deactivation of I^* by HI , i.e.,



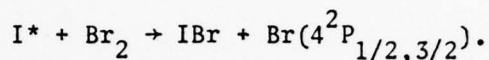
where the chemical exchange of the iodine atoms results in an enhancement of the overall rate. Such exchange reactions have been suggested in the case of the efficient vibrational deactivation of vibrationally excited hydrogen halides by halogen atoms.²⁶ Indeed, the present experimental results may be used to assess the effect of electronic excitation on the rate of chemical reaction. Thus, if the activation energy for the reaction of ground state iodine atoms with HBr



is assumed to be equal to the endothermicity, it is possible to estimate the fraction of electronic excitation energy made available to the collision partners to surmount the activation barrier. If the cross-section for a gas kinetic I-HBr collision is ca 16 \AA^2 (based on Xe-Kr collision diameters)²⁷ and the nominal steric factor is taken as unity, the observed rate constant for (1), 1.5×10^{-13} , may be interpreted as being associated with a maximum activation energy of 4.3 kcal. Thus, 11.9 kcal or 55% of the 21.7 kcal excitation energy associated with $\text{I}(5^2\text{P}_{1/2})$ is made available to the collision complex. This reflects a lower limit, however, for the actual preexponential factor is < 1 .

The absence of a large energy barrier to reaction may now be viewed in the context of simple models based on the electronic structure of the I-HBr collision complex. Turning first to the one-electron valence bond approach developed⁷ to explain the efficient quenching of $\text{Br}(4^2\text{P}_{1/2})$ by HI where neither adiabatic nor non-adiabatic chemical reaction appears to play a significant role, it seems clear that a serious discrepancy is raised by the current results. Inspection of Fig. 4 of reference 7, would suggest that the initial approach of I^* to HBr should take place on a strongly repulsive

surface. Therefore, any reactive process which requires a close approach of the reactants should display a significant activation barrier and, in addition, would be expected to be relatively inefficient with respect to long-range processes such as energy transfer. The applicability of this simple model has been further challenged by recent experimental work²⁸ which demonstrated that the original studies⁷ failed to account for the rapid reaction



This reaction would have made the adiabatic route for deactivation of $Br(4^2P_{1/2}) + HI$ very difficult to detect under the conditions of the earlier experiments.

Clearly, a more detailed examination of the potential surfaces governing the I^* -HBr interaction is warranted by the present observation of an efficient channel (1) leading to $Br + HI$. In order to discuss the nature of the potential hypersurfaces governing the dynamics of the deactivation process, it is necessary to consider each of the three surfaces correlating with $X(^2P_{3/2,1/2}) + HY$. Accepting the suggestion of Bergmann, *et. al.*,⁷ that only the lowest surface correlating with $X(^2P_{3/2}) + HY$ is attractive, we now include the effect of the presence of vibrationally excited virtual levels of the molecular reactant, HBr. This extension was suggested by Donovan and coworkers⁶ and follows from the classical representation²⁹ of adiabatic potential surfaces corresponding to vibrationally excited states as being similar to those correlating with the ground state, but being displaced upward in energy by $h\nu_{vib}$. The nature of the potential hypersurfaces near the nuclear arrangement corresponding to reactant $I + HBr$ is presented schematically in Figure 7. Here, the symmetry of the curves

are given for the cases of weak spin-orbit coupling and symmetries of the intermediate complex which are either planar ($^2A'$ or $^2A''$) or axial ($^2\Sigma^+$, $^2\Pi_{1/2,3/2}$) as well as strong spin-orbit coupling (all surfaces of $E_{1/2}$ representation³⁰). Surfaces designated as type 1 lead to $\text{Br} + \text{HI}$ and are characterized by an attractive interaction. Surfaces 2 and 3 are non-bonding at large internuclear separations and possibly repulsive at close approach.

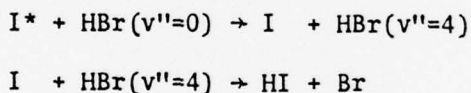
The regions of greatest concern to the present discussion center around the crossings of the hypersurface correlating with the reactants $\text{I}^* + \text{HBr}$ (type 3) and those correlating with $\text{I} + \text{HBr}$ ($v''=3$) (type 2) and $\text{I} + \text{HBr}$ ($v''=4$) (type 1). These crossings are avoided for the case of j, Ω coupling where all surfaces are represented by $E_{1/2}$ in the extended $C_{\infty v}$ point group. As chemical reaction and not physical quenching has been shown to be the dominant route for collisional deactivation of I^* by HBr , clearly the region near the crossing (point A) between the surface correlating with $\text{I}^* + \text{HBr}$ ($v''=0$) and that correlating with $\text{I} + \text{HBr}$ ($v''=4$) must be of primary importance. The failure to observe a significant channel to ground state iodine atoms suggests that the crossing between the surface emanating from $\text{I}^* + \text{HBr}$ ($v''=0$) with the surface correlating with $\text{I} + \text{HBr}$ ($v''=3$) (point B) must occur at an energy not available to a significant fraction of the colliding reactants at 295°K. As the crossing at A is avoided, it is perhaps surprising that the overall rate constant for reaction, $1.5 \pm 0.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, is not larger. Of course, a small activation barrier to reaction may indeed be present, 4 kcal being the maximum possible. However, it must also be recalled that the probability for non-adiabatic passage through the avoided crossing at point A must be relatively large. This is due to the need to include the vibrational overlap between the initial and final states in the calculation of the overall matrix element, $V(R_A)$, for transition from the $v''=0$

level of the type 3 surface to the $v''=4$ level of the type 1 surface,

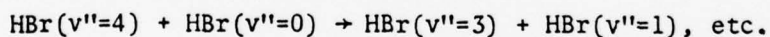
$$V_{0,4}(R_A) = V_{el}(R_A) (q_{0,4}(R_A))^{1/2}$$

where V_{el} is the electronic part of the matrix element at R_A and q represents the Frank-Condon factor for the vibrational overlap.³¹ The rate constants for deactivation of I^* by HBr and DBr, $k_{HBr}/k_{DBr} = 4.7$, is not inconsistent with this interpretation as the matrix element would involve $q_{0,5}$ which would be significantly smaller than the Frank-Condon factor for the 0-4 transition. The magnitude of the potential barrier to the region of avoided crossing at A and B will be assessed in temperature-controlled experiments to be undertaken in this laboratory.

It is interesting to note that the proposed model discussed above suggests that the products of (1) are formed in a concerted reaction following initial production of HBr ($v''=4$) + I. The observed reaction cannot be the result of the following two-step mechanism



as the second step would be in competition with the rapid vibrational process



and $[HBr] \sim 10^4 - 10^5 \times [I]$. The nascent energy distribution of the $HI(v''=n) + Br$ should correspond to that which would have been obtained following the reaction of vibrationally excited HBr with ground state iodine atoms. Observation of the vibrational energy disposition in the products of this reaction would greatly facilitate the evaluation of the proposed mechanism. Furthermore, such an experiment would permit the

assessment of the role of reactant vibrational energy in chemical processes.

It should be noted that failure to observe the ground state iodine atom suggests that there is no remaining thermal barrier to reaction to form $\text{Br} + \text{HI}$ once the path of avoided crossing is taken at point A.

Acknowledgment

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Table I. Rate Coefficients for Deactivation of $I(5^2P_{1/2})$ at 295°K.

Q	K_Q ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)	Ref.
CH_4	$1.0 \pm 0.2 \times 10^{-13}$	a
	$1.1 \pm 0.5 \times 10^{-13}$	b
	$9.7 \pm 0.3 \times 10^{-14}$	This work
C_3H_8	$1.7 \pm 0.1 \times 10^{-13}$	a
	$1.9 \pm 0.3 \times 10^{-13}$	b
	$1.6 \pm 0.1 \times 10^{-13}$	This work
HBr	$1.3 \pm 0.1 \times 10^{-13}$	c
	$1.6 \pm 0.1 \times 10^{-13}$	d
	$1.5 \pm 0.1 \times 10^{-13}$	This work
DBr	$\leq 4.9 \pm 0.3 \times 10^{-14}$	c
	$3.1 \pm 0.2 \times 10^{-14}$	This work

a. D. Husain and J.R. Wiesenfeld, Trans. Faraday Soc., 63, 1349(1967).

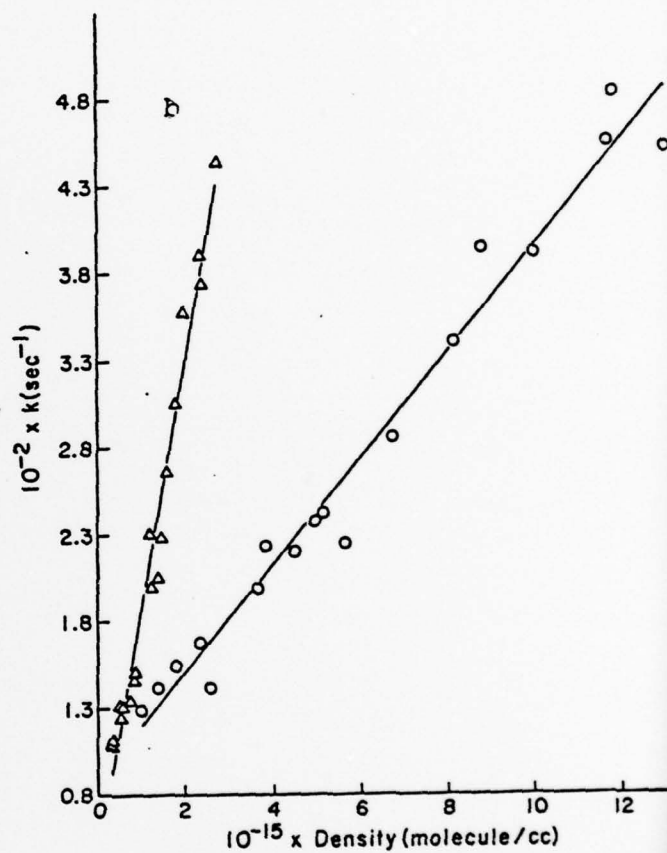
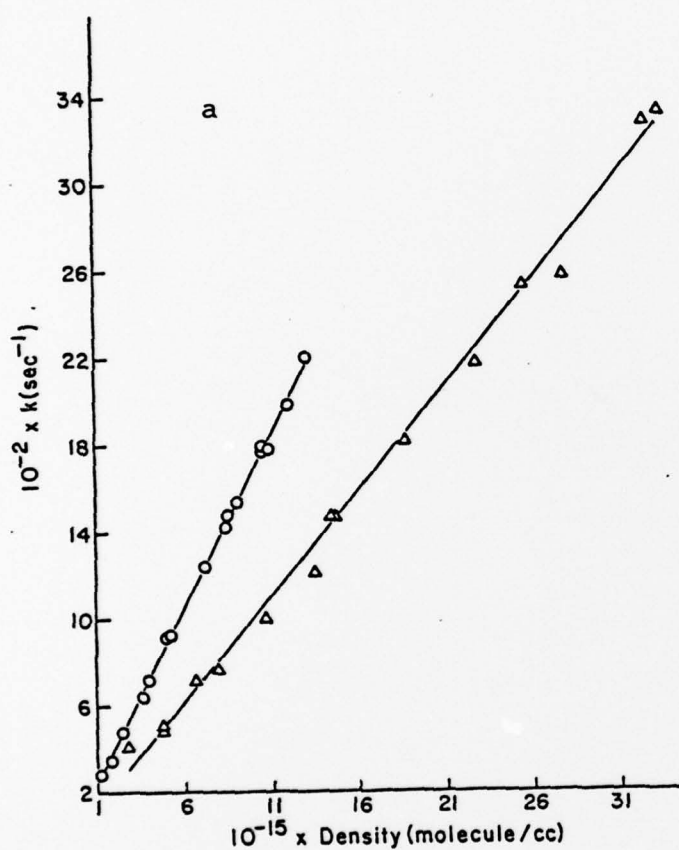
b. J.J. Deakin and D. Husain, J. Chem. Soc. Faraday II, 68, 41(1972).

c. Reference 6.

d. Reference 8.

Table II. Fraction of Deactivating Collisions
Resulting in Chemical Reaction.

Q	Λ (equation 10)
CH_4	0.03 ± 0.11
C_3H_8	0.03 ± 0.16
HBr	0.96 ± 0.12
DBr	0.94 ± 0.13



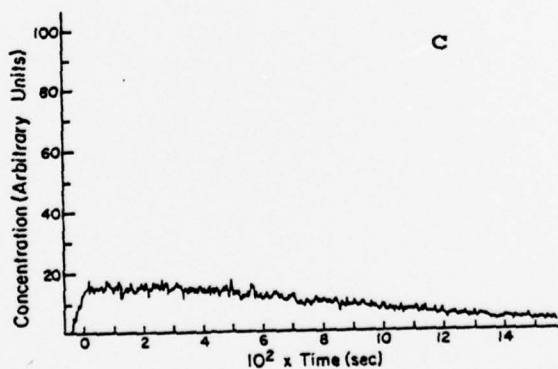
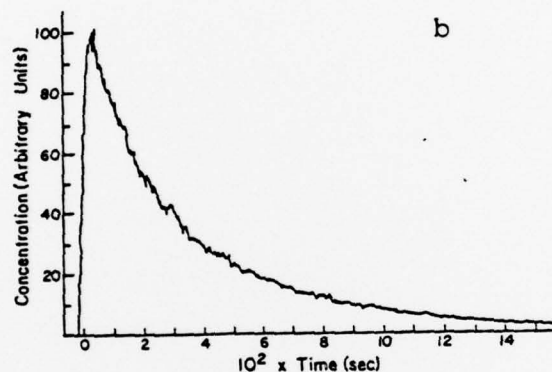
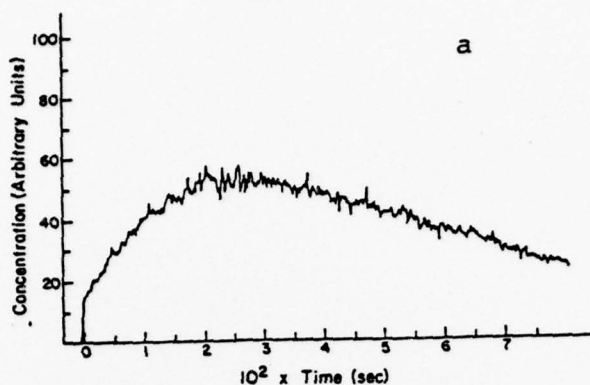
1. Plots of pseudo-first order rate constants for removal of $\text{I}(5^2\text{P}_{1/2})$ vs. density of deactivating gas.

a. O C_3H_8

Δ CH_4

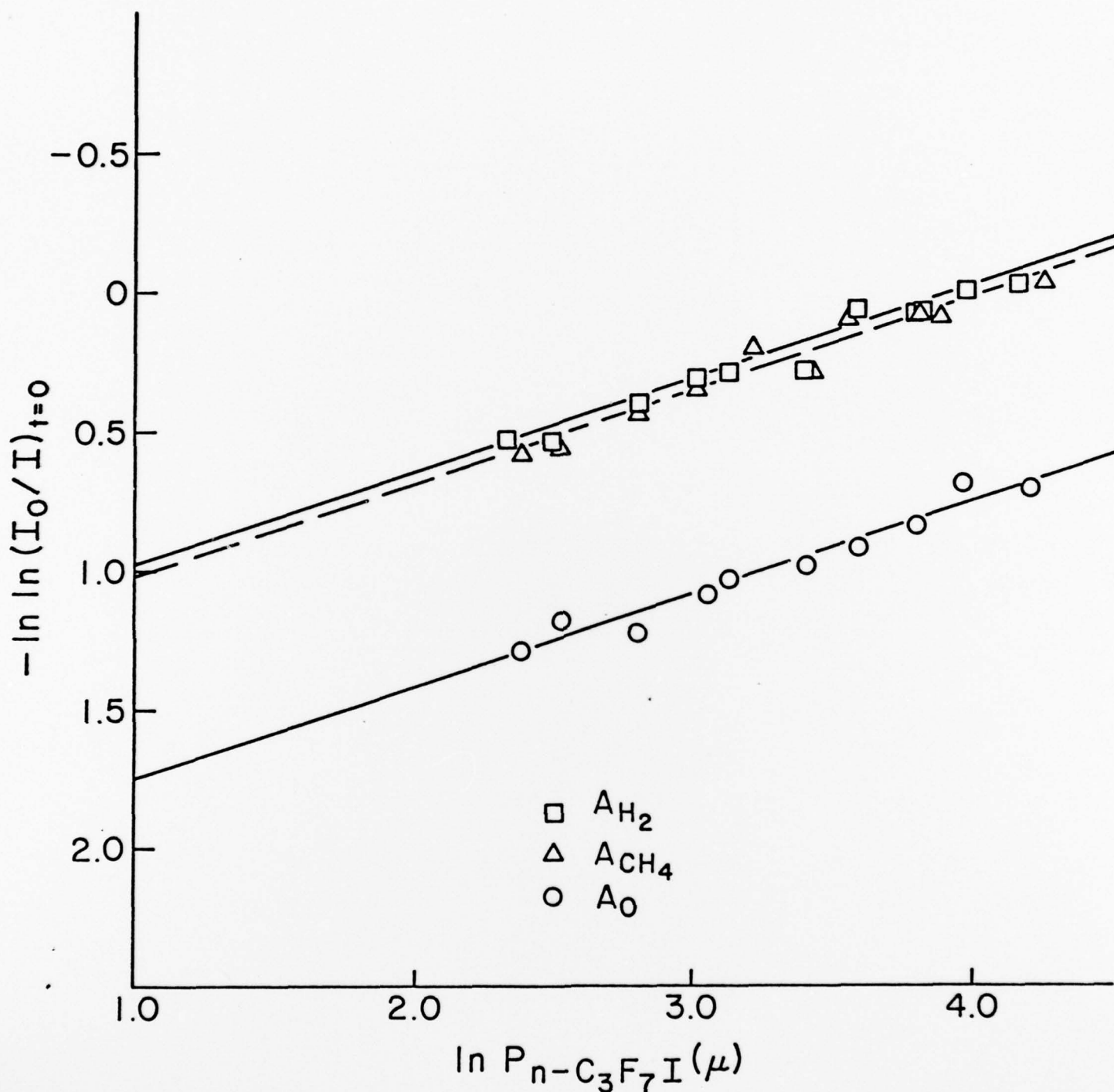
b. O DBr

Δ HBr

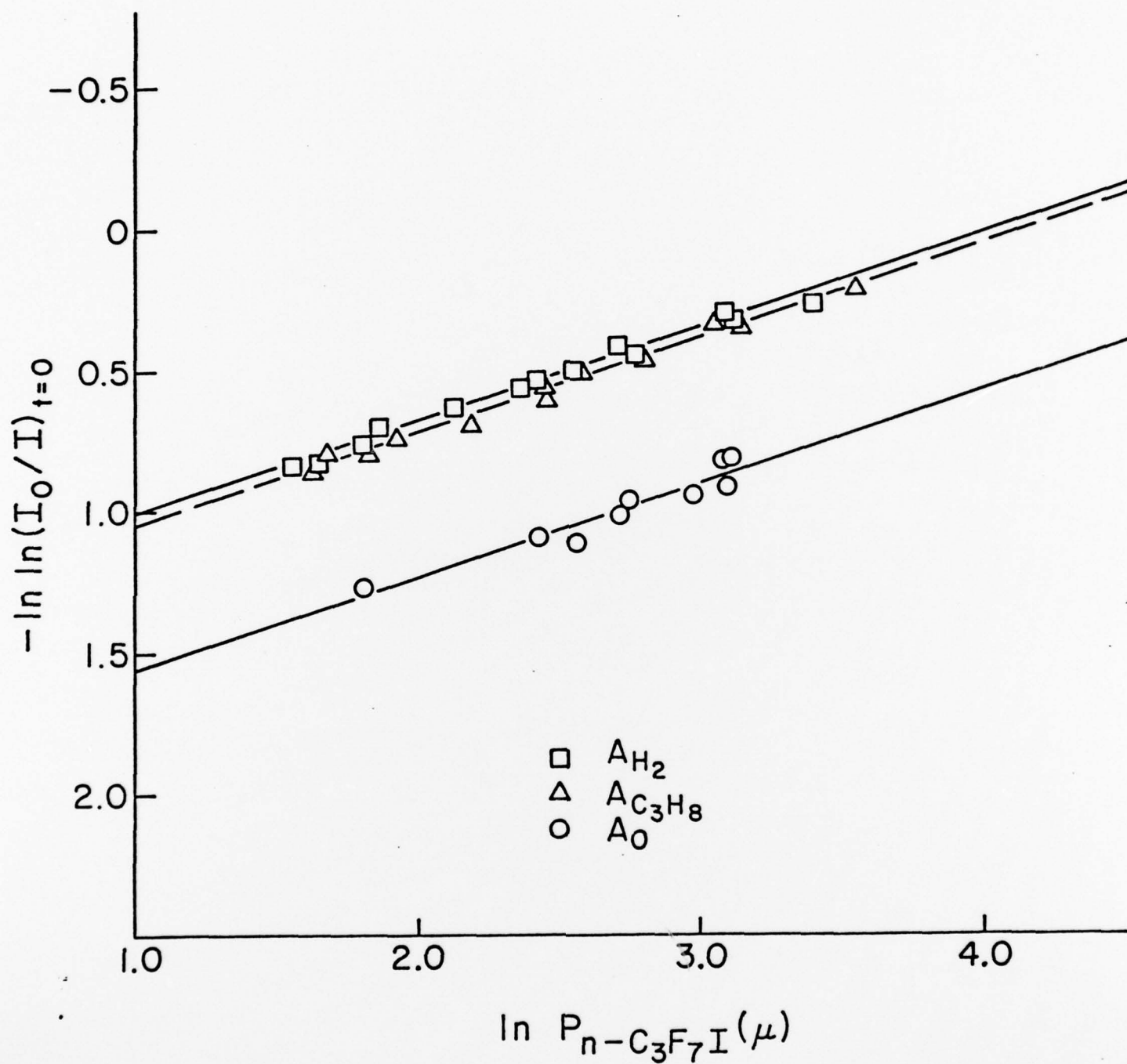


2. Temporal profiles of $I(5^2P_{3/2})$ following photolysis of a solution of $n-C_3F_7I$ in argon ($P_{n-C_3F_7I} = 0.019$ torr, $P_{Ar} = 60$ torr, $E = 100J$). The different solutions included:
 - a. no added deactivating gas;
 - b. 0.37 torr H_2 to quench all $I(5^2P_{1/2})$ rapidly to $I(5^2P_{3/2})$;
 - c. 0.25 torr HBr, a deactivator of unknown reactivity in the presence of $I(5^2P_{1/2})$.

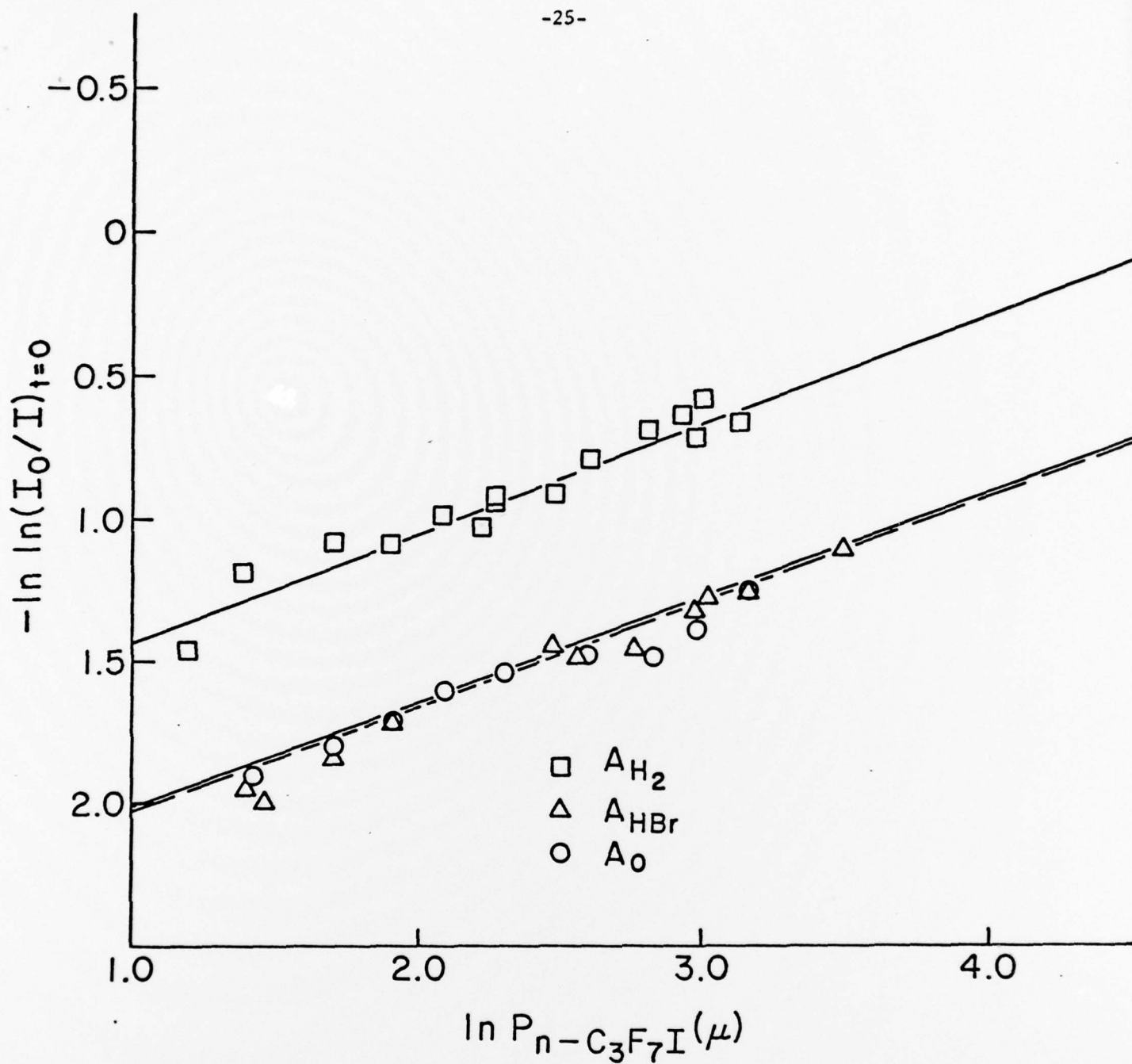
These traces, each representing the average of 16 kinetic runs, demonstrate the dominance of reaction (1) in the deactivation of $I(5^2P_{1/2})$ by HBr.



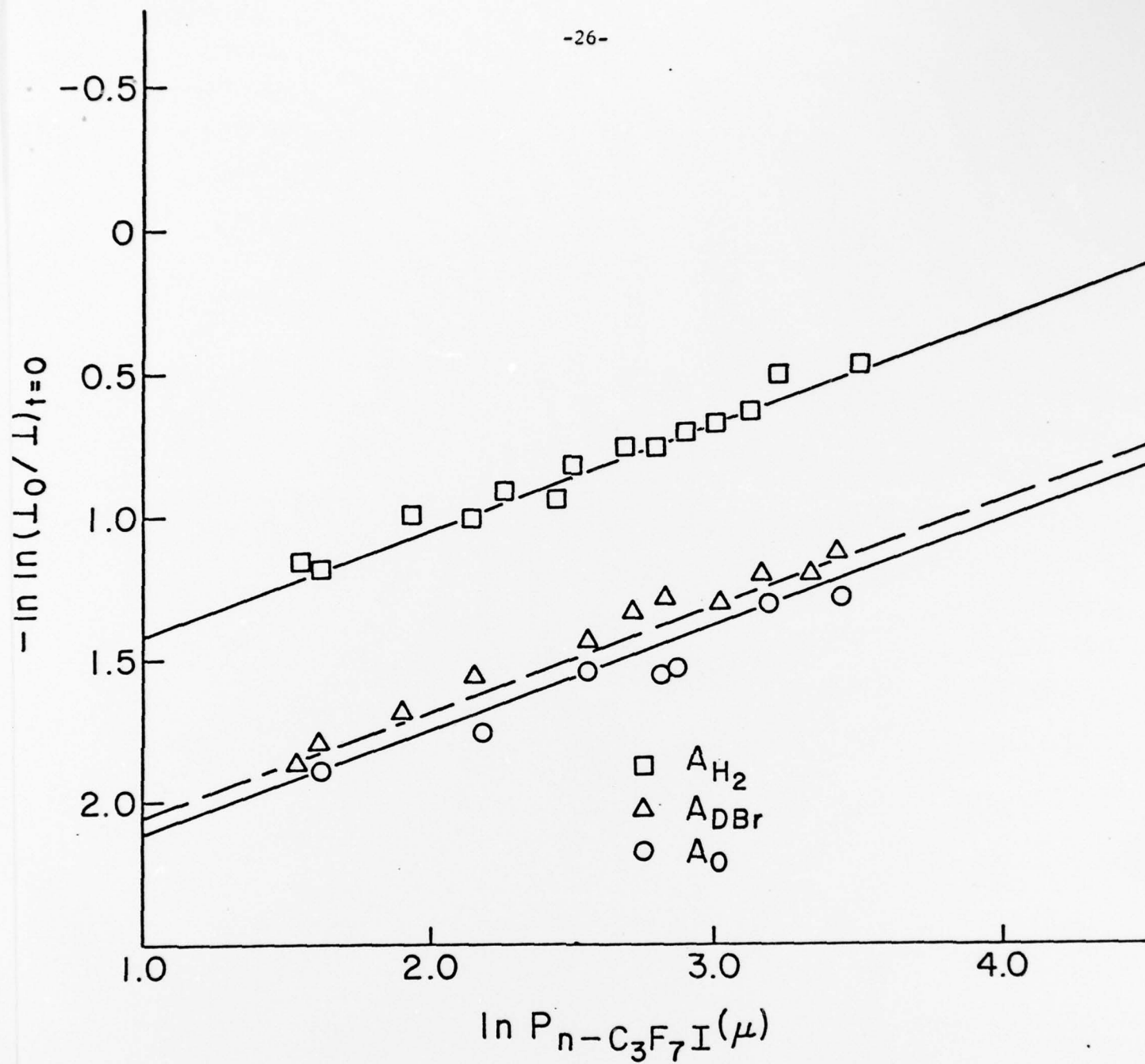
3. Plot of $-\ln \ln(I_0/I)_{t=0}$ vs. $\ln P_{n-C_3F_7I}$ demonstrating the validity of equations (12) and (13). The essential overlap of points collected in the presence of H_2 and CH_4 suggests that reaction plays no role in the deactivation of $I(5^2P_{1/2})$ by CH_4 . For the sake of clarity, only a random selection of the actual data taken is presented here.



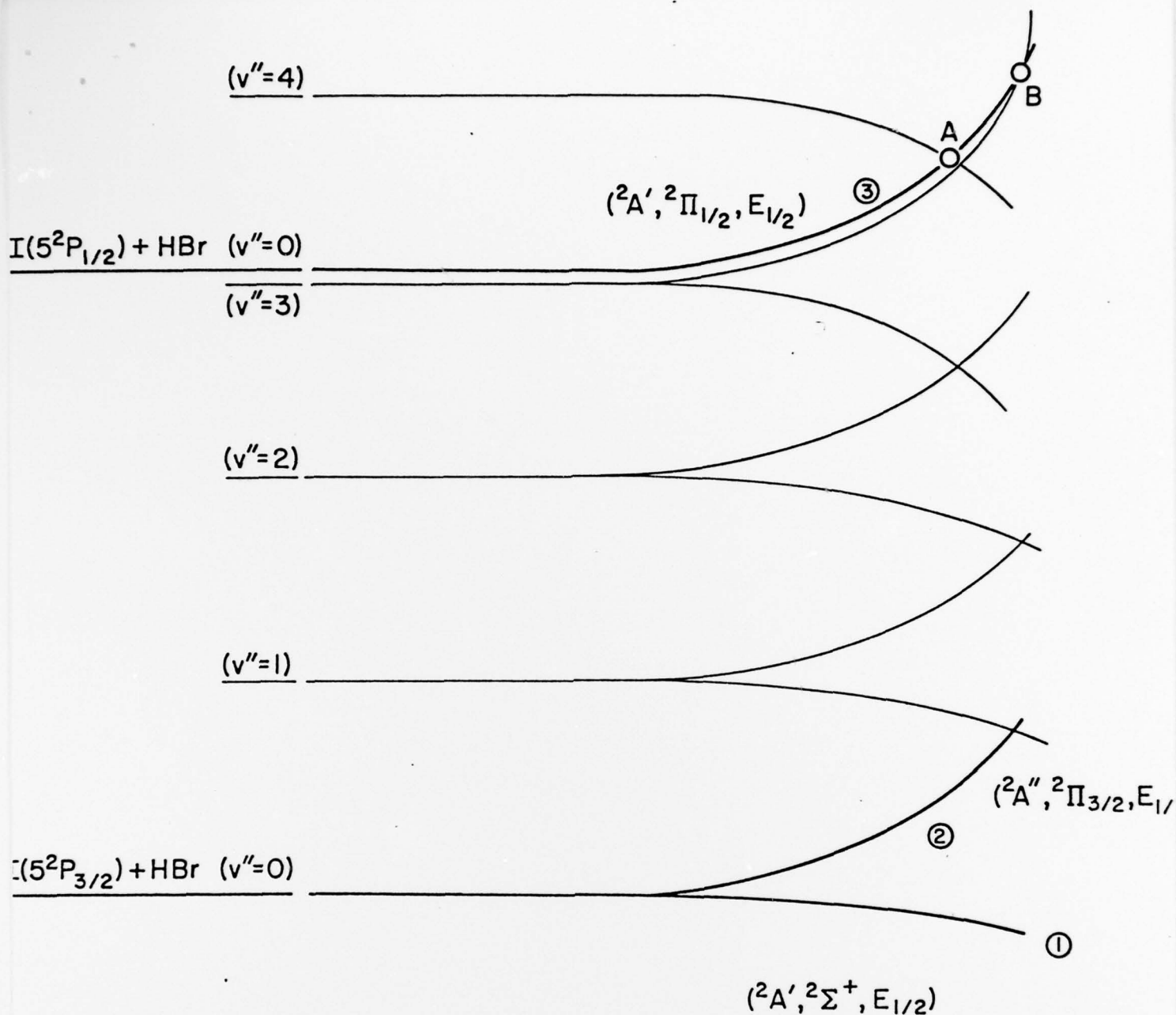
4. As for Figure 3, but the deactivating molecule is C_3H_8 . No significant degree of reactive deactivation is observed.



5. As for Figure 3, but the deactivating molecule is HBr. The agreement of the initial absorbances obtained in the absence of any added quencher (Fig. 2a) and the presence of HBr (Fig. 2c) is the result of chemical reaction between $I(5^2P_{1/2})$ and the deactivating gas.



6. As for Figure 3, but the deactivating molecule is DBr. Once again, chemical reaction is the major channel for collisional deactivation.



7. Schematic drawing of the potential surfaces governing the interaction between iodine atoms and HBr. Type 1 surfaces correlate to $Br(4^2P_{3/2}) + HI$ via a surface which is essentially bonding. Type 2 surfaces correlate with the same products but are presumably non-bonding at large internuclear distances and somewhat repulsive at close approach. The type 3 surface correlates with $Br(4^2P_{1/2}) + HI$ and is also non-bonding in nature. At point A, it undergoes an avoided crossing (for the case of j, Ω coupling) with the virtual surface correlating with vibrationally excited HBr; this type 1 surface leads to chemical reaction. The avoided crossing at B, which is suggested here to occur at higher energies, leads to formation of $I(5^2P_{3/2})$ and is presumably of no significance in the present reaction.

Figure Captions

1. Plots of pseudo-first order rate constants for removal of $I(5^2P_{1/2})$ vs. density of deactivating gas.
 - a. O C_3H_8
 Δ CH_4
 - b. O DBr
 Δ HBr

2. Temporal profiles of $I(5^2P_{3/2})$ following photolysis of a solution of $n-C_3F_7I$ in argon ($P_{n-C_3F_7I} = 0.019$ torr, $P_{Ar} = 60$ torr, $E = 100J$). The different solutions included:
 - a. no added deactivating gas;
 - b. 0.37 torr H_2 to quench all $I(5^2P_{1/2})$ rapidly to $I(5^2P_{3/2})$;
 - c. 0.25 torr HBr, a deactivator of unknown reactivity in the presence of $I(5^2P_{1/2})$.

These traces, each representing the average of 16 kinetic runs, demonstrate the dominance of reaction (1) in the deactivation of $I(5^2P_{1/2})$ by HBr.

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